ropy of the repulsive wall of the HF + inert gas potentials remains unchanged with varying heights on the wall, and also for different inert gases.[13]

The state-to-state cross sections reported here have additionally been found to scale according to a relationship based on the energy corrected sudden approximation.[14] It was necessary to fit upward $(J<J')$ and downward $(J>J')$ cross sections separately, the effective collision length being $l_c = 1.3$ Å and 9 Å, respectively.

Details of the experimental technique and further results will be presented in a forthcoming paper.

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Wavelength and vibrational-state dependence of photoelectron angular distributions. Resonance effects in 5 σ photoionization of CO[a)]

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The dynamics of molecular photoionization have recently been shown[1] to vary rapidly with internuclear separation in the presence of a shape resonance. In a prototype calculation[1] on the $3\sigma_g$ photoionization channel of N_2, the σ_u resonance shifted by > 10 eV and exhibited large, asymmetric variations in intensity and width over a range in R spanning the ground vibrational state of N_2. This leads to a breakdown in the Franck–Condon (FC)

separation and was predicted[1] to cause non-FC vibrational intensities and v-dependent photoelectron angular distributions. The effect of shape resonances on vibrational branching ratios has been confirmed experimentally in connection with the analogous f-wave–dominated σ resonances in the 5σ channel[2] of CO and the $3\sigma_g$ channel[3] of N_2. By contrast, the available data[4–9] on vibrationally resolved photoelectron angular distributions in

$$CO^+ \quad X^2\Sigma^+$$
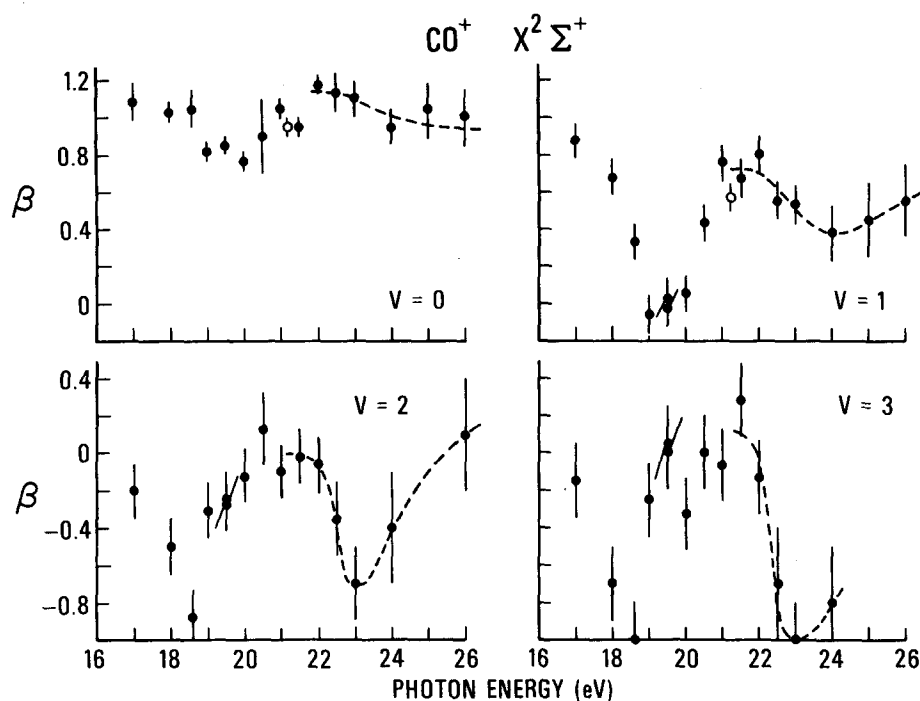

FIG. 1. Photoelectron asymmetry parameters for the $v = 0-3$ vibrational levels of $CO^+ X^2\Sigma^+$ in the range 16 eV $\leq h\nu \leq 26$ eV. The open circles are data by Hancock and Samson (Ref. 7) using He I resonance radiation. The dashed lines are hand drawn to illustrate the discussion in the text.

shape-resonant channels is too fragmentary to establish the pattern of the shape resonance effect. Here we report measurements of vibrationally resolved photoelectron angular distributions for the 5σ channel in CO, performed in the range 16 eV $\leq h\nu \leq$ 26 eV utilizing synchrotron radiation, in order to establish the gross pattern of variation of the asymmetry parameter β in the vicinity of the σ shape resonance at $h\nu \sim 24$ eV.[10–15] As discussed below, unresolved autoionization structure, also capable of producing v-dependent βs, is also observed and partially masks the expected shape-resonance effect. Although mainly a compilation in this particular study, detailed studies of resolved autoionization effects are of great importance and are being pursued separately.

The instrument used in this work is described in detail elsewhere.[2,3,16] Briefly, it consisted of the high-flux, 2 m, normal-incidence monochromator[17] at the Synchrotron Ultraviolet Radiation Facility (SURF-II) of the National Bureau of Standards, together with a rotatable, 2 in. mean-radius hemispherical electron energy analyzer.[18] The combination of 0.8 Å photon bandpass and ~100 meV analyzer resolution resulted in an overall resolution sufficient to resolve the 0.27 eV vibrational structure in the $CO^+ X^2\Sigma^+$ band. To determine the photoelectron asymmetry parameter β, three spectra spanning the $v = 0-3$ peaks in the $X^2\Sigma^+$ band of CO^+ were recorded at $\theta = 0°$, 45°, 90°. The error bars in Fig. 1 denote the uncertainties in a computer fit to the vibrational peaks in the experimental spectrum plus the differences in β values derived from the (0°, 45°) and (0°, 90°) sets of data.

The wavelength dependence of the βs for the first four vibrational levels of $CO^+ X^2\Sigma^+$ is given in Fig. 1. We note that the $v = 0$ curve is rather flat and agrees, within combined stated errors, with the vibrationally unre-

solved data of Marr et al.[19] and the multiple-scattering calculations of Wallace et al.[20] and that a systematic tendency to be slightly higher than the vibrationally unresolved data[19] reflects the small admixture of the higher vibrational levels which were resolved in this work. Also note the good agreement with the He I data of Hancock and Samson[7] for $v = 0$ and 1. In interpreting the gross patterns in the data, we follow the discussion of the vibrational branching ratios in Ref. 2 by tentatively defining two spectral regions with different dominant effects. Below ~21 eV, we presume the main vibrational effects are caused by unresolved autoionization structure and threshold effects associated with the $B^2\Sigma^+$ state of CO^+ at 19.7 eV (although shape resonance effects are also likely to extend into this region). Above 21 eV, we assume[21] the structure is caused mainly by the shape resonance centered at ~24 eV.[10–15] Focussing briefly on the "autoionization" region below ~21 eV, we note that a broad dip occurs in β for each vibrational level, with a successively deeper minimum centered at ~19 eV. Although this is similar to the structure in the "shape-resonance" region discussed below, it is significantly different in that this gross structure is comprised of unresolved series of autoionizing structures. Separate studies on a much finer energy mesh are being pursued to study details of individual autoionizing structures. Above ~21 eV, we believe the present data are the first to map the pattern of variation of v-dependent βs directly reflecting the effects of a shape resonance. The following pattern emerges, as illustrated by the hand-drawn dashed lines in Fig. 1: First, the $v = 0$ curve is relatively flat at $\beta \sim 1$. The vibrationally unresolved data[19] (dominated by the $v = 0$ component) exhibits a broad, shallow dip at ~28–30 eV, in agreement with theory.[20] Second, the $v = 1$ curve is substantially lower above 22 eV and exhibits a discernible minimum at ~24 eV, the position of the shape resonance. Third, the $v = 2$

curve continues the pattern of a deeper dip (note the ordinate scale change on the lower part of Fig. 1) centered at lower photon energy. Finally, the $v = 3$ curve, although of marginal statistical significance due to the vanishingly small branching ratio, appears to indicate a deeper plunge. We emphasize that our interpretation of this pattern as a shape resonance effect is tentative, as we cannot definitely rule out influence by weak autoionization structure in this spectral range[21]; however, the interpretation is plausible in view of related definitive work on vibrational branching ratios, particularly Refs. 1 and 3, and qualitative agreement of the present results with recent multiple-scattering model calculations[22] further supports this interpretation.

To summarize, we have observed v-dependent angular distributions in the 5σ channels of CO, which we interpret as arising from unresolved autoionization structure below ~ 21 eV and from the σ shape resonance above this energy. Although the shape resonance will probably affect the vibrational state βs all the way to threshold, this would probably take the form of a general shift of $\beta(v)$ and would be masked by the autoionization structure, as was observed in the earlier study[2] of vibrational branching ratios. Of central interest here is the isolated shape resonance effect above $h\nu \sim 21$ eV, taking the form of a dip in the β curve which is successively lower in magnitude and photon energy with increasing vibrational quantum number. This is a very noteworthy contrast with the closely related case of the $3\sigma_g$ channel in N_2 where theory predicts[1] a very different pattern, in particular that $\beta(v = 1) > \beta(v = 0)$ over the first 25 eV above threshold. Clearly both theoretical studies of the present observation and improvements in the quality and extent of the experimental evidence is needed to establish a clear understanding of these newly uncovered shape-resonance-induced vibrational effects.

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